Method for reducing the extractives content of high-yield pulps and method for producing bleached high-yield pulps

Field of the invention

The present invention relates to a method for reducing the extractives content of high-yield mechanical pulps. The invention also relates to a method for producing bleached high-yield pulps having a reduced content of extractives.

Description of the prior art

Extractives are known constituents of wood and pulp species that are extractable with organic solvents. The most predominant chemical groups found in extractives are fatty and resin acids, terpenes, phytosterols and phenolic compounds. Extractives are found esterified, glycosylated and nonderivatized. The most problematic extractives in wood are mainly the oleophilic compounds. They are fatty acids, resin acids, terpenes and sterols and their function is to protect the tree by preventing attacks from germs, funguses etc. Scandinavian softwoods contain approximately 1.5% extractives by weight while hardwoods of the temperate zone usually contain 2-2.5% by weight. Generally, the problematic extractives are commonly referred to as pitch. Problems are usually found in high shear force areas and when the temperature, pH or pitch concentration changes.

Common detrimental effects from pitch in different areas are as follows. In bleach plants, deposits are formed and may also increase consumption of chemicals. In the final product spots and high level of extractives are found.

A modern bleaching process for mechanical pulps includes often high-consistency peroxide bleaching (PHC). After peroxide bleaching the pulp is often diluted with white water coming from the paper machine and after that the pulp slurry is dewatered. This washing step reduces carry-over of anionic trash to paper machine and also allows recirculation of residual peroxide. Alkaline peroxide oxidizes and removes quite efficiently extractives from the pulp. However, if the pulp in the bottom of PHC bleach tower or after PCH bleaching is diluted with white water the extractives can re-precipitate in the surface of pulp or process equipment due to lower pH of the water, high hardness or electrolyte (salt) concentration. Precipitated extractives will be transferred in the fiber surface to the paper machine leading to

problems in wet end and paper quality. When the PHC wash filtrate is recirculated back to earlier stages of the process, the extractives, possibly found in the wash filtrate, can be precipiteted in the process equipment or fibers in acidic or neutral environment.

US 4 363 699 describes a process for stabilizing alkaline solutions of peroxidic compounds used for bleaching wherein an alkaline salt of a poly-alfa-hydroxy-acrylic acid is added to the solution as a stabilizer. The stabilized solutions can be used for the bleaching of paper pulps and textiles. When bleaching textiles, the bleaching solution may contain a wetting agent which is a surface active agent.

US 4 963 157 describes a method of bleaching a cellulosic fiber material, especially cotton with hydrogen peroxide. The method comprises impregnating the fiber material with a bleaching solution containing hydrogen peroxide and a stabilizer. The stabilizer comprises poly-alfa-hydroxyacrylic acid or a salt thereof or the polylactone corresponding thereto, and an organic phosphonic acid or a salt thereof.

DE 3423452 discloses a solution for avoiding the use of water glass comprising a stabilizing mixture of a poly-alfa-hydroxyacrylic acid (PHAA) and a water soluble homopolymer of acrylic or methacrylic acid or a copolymer of acrylic acid and/or maleic acid. The salts, especially the sodium salt of PHAA and the sodium salt of the polycarboxylate polymer are mixed together. Chelating agents can be added to the mixture and thus an improved stabilizer mixture for bleaching processes is obtained. According to DE 3423452 the bleaching process is carried out by using an alkaline peroxide bleaching liquor containing said stabilizing mixture.

Summary of the invention

The invention is based on the fact that the extractives are more soluble in alkaline conditions and thus, when the pulp is diluted with dilution water, for example white water after bleaching, the extractives may redeposit on the fiber surfaces especially when the pH of dilution water is lower that that of pulp coming out from bleaching tower. According to the present invention it has been found that certain surface-active agents can inhibit precipitation of extractives and thus keep them in water phase. Then the extractives can be washed off the pulp at next dewatering press which in turn leads to reduced extractives content in the pulp. Since the extractives are dispersed and the particles are stabilized, there is no re-precipitation of extractives when the filtrate is re-circulated to the earlier process stages.

The invention is especially advantageous when the pulp is bleached without silicate as stabilizer, since it has been noticed that silica has some dispersing efficiency against extractives. However, the invention works also well in the presence of silicate.

Detailed description of the invention

According to the present invention there is provided a method for reducing the content of extractives of a high-yield pulp in a peroxide bleaching stage, said stage including peroxide bleaching and a subsequent dewatering or washing, said method comprising contacting the pulp in the peroxide bleaching with an organic stabilizer and in or after the peroxide bleaching with a surfactant, and thereafter subjecting the bleached pulp to said dewatering or washing for removing extractives along with the aqueous phase.

In this context the peroxide bleaching stage includes peroxide bleaching of the pulp, optionally dilution of the pulp, and dewatering or washing of the pulp.

According to the present invention there is also provided a method for producing bleached high-yield pulp having a reduced content of extractives comprising bleaching high-yield pulp with peroxide, the pulp being contacted with an organic stabilizer during the peroxide bleaching and with a surfactant during the peroxide bleaching or after the peroxide bleaching, and dewatering or washing the bleached pulp for removing extractives along with the aqueous phase and for producing bleached high-yield pulp having a reduced content of extractives.

The extractives to be removed from the pulp according to the present invention originate from the wood pitch. The extractives include fatty acids, resin acids, terpenes, phytosterols and phenolic compounds in esterified, glycosylated and/or nonderivatized form. The most problematic extractives include fatty acids, resin acids, triglycerides, steryl esters, sterols and lignans.

The organic stabilizer and the surfactant can be added separately or these chemicals can be mixed beforehand with the bleaching solution. Furthermore the organic stabilizer and the surfactant can be added simultaneously or separately as one chemical mixture, i.e. product.

The organic stabilizer and the surfactant can be added to the pulp in the peroxide bleaching or before the peroxide bleaching.

It is also possible to add the surfactant to the pulp after the peroxide bleaching. In that case the surfactant can be added to dilution water which is added to the pulp between the peroxide bleaching and the dewatering or washing. The dilution water can be white water circulated from the paper machine.

The organic peroxide stabilizer used in the methods of the invention is preferably a polymeric stabilizer, such as a poly-alfa-hydroxyacrylic acid or a salt thereof or the corresponding polylactone, a homopolymer of acrylic acid, methacrylic acid or maleic acid or a copolymer of acrylic acid and/or methacrylic acid with an unsaturated dicarboxylic acid. The polymeric stabilizer can also be a mixture of the poly-alfa-hydroxyacrylic acid and the homopolymer and/or the copolymer. The unsaturated dicarboxylic acid is preferably maleic acid. The salt of the poly-alfa-hydroxyacrylic acid is preferably a sodium, potassium or ammonium salt. The poly-alfa-hydroxyacrylic acid can have a molecular weight of at least 5000, preferably at least 10000, and more preferably at least 15000 (calculated as the sodium salt of the PHAA). The homopolymer and the copolymer can have a molecular weight of at least 4000, preferably at least 10000, and more preferably at least 20000.

The organic stabilizer can also be a phosphonic acid or a salt thereof. The salt is preferably a sodium, potassium or ammonium salt. Suitable phosphonic acids are for example the (poly)aminophosphonic acids, such as aminotri(methylenephosphonic acid), ethylenediaminetetra(methylenephosphonic acid), i.e. EDTMPA, or diethylenetriaminepenta(methylenephosphonic acid), i.e. DTPMPA.

In addition to said organic stabilizer it is possible to introduce another stabilizer. This other stabilizer can be an alkaline earth metal compound such as a magnesium and/or calcium compound. The alkaline earth metal compound can be in the form of a salt, such as a sulphate, chloride or any other water soluble salt or in the form of a complex with a polymer or a chelating agent. A preferred alkaline earth metal salt is magnesium sulphate.

The amount of the organic stabilizer is preferably from 0.1 kg to 5 kg per ton dry pulp, more preferably from 0.25 kg to 3 kg per ton dry pulp, and even more preferably from 0.5 kg to 3 kg per ton dry pulp.

The surfactant used in the methods of the invention can be an anionic surfactant, such as naphthalene sulphonate or lignosulphonate, or a non-ionic surfactant, such as an O/W emulsifier, f. ex. a fatty alcohol ethoxylate or alkyl phenol ethoxylate.

Also a mixture of the anionic and non-ionic surfactants can be used. Defoamers can be used in combination with the surfactant(s) to prevent foaming.

The amount of the surfactant is preferably from 0.005 kg to 2 kg per ton dry pulp, more preferably from 0.05 kg to 1 kg per ton dry pulp.

The methods of the invention are used in bleaching high-yield mechanical pulps, like groundwood pulps, stone groundwood pulps, pressure groundwood pulps (GW, SGW, PGW), refiner mechanical pulps (RMP), thermomechanical pulps (TMP) and chemithermomechanical pulps (CTMP, APMP).

In the peroxide bleaching hydrogen peroxide is preferably used as the bleaching agent. Other chemicals such as bleaching stabilizers, chelating agents and/or magnesium sulphate can be used in the bleaching. Especially advantageous is to add the chemicals before bleaching or at the same time with bleaching chemicals. If there are several bleaching stages, the chemicals can be added in any of them or in several stages.

The residence time in the bleaching can vary within a wide range, from 30 to 240 minutes, preferably from 45 to 180 minutes and most preferably from 60 to 120 minutes. The residence time will also depend on the temperature used in the bleaching.

The bleaching of high-yield pulps can be carried out at a temperature of 30-90°C, preferably at a temperature of 50-90°C. The bleaching can be carried out at a consistency of choice, but it is most preferably to carry out the bleaching at a high consistency, i.e. about 30% or higher. Bleaching can also be carried in two stages with a dewatering stage between the stages.

The pH in the alkaline bleaching of the invention can be from 7 to 14, preferably from 8 to 11. The ratio between the alkali, typically sodium hydroxide, and hydrogen peroxide can vary in a wide range, depending on raw materials and degree of bleaching. Also alternative alkali sources, like sodium carbonate, can be utilized.

The present invention will be illustrated by following examples. The percentages are % by weight unless otherwise specified. "kg/t" means kilograms per ton dry pulp. "Cs" means consistency. "**P**" stands for peroxide stage.

Examples

Comparative example

The purpose of this comparative example is to clarify the problem to be solved by the invention. TMP pulp (spruce) was bleached in high consistency with peroxide using waterglass or poly-α-hydroxy acrylate (PHAA) as stabilizer. Subsequently the pulp was diluted with ion exchanged water and then dewatered to consistency of 30%. The detailed experimental data is shown in table below.

	P	P
T, °C	70	70
t, min	120	120
Cs, %	27	30
Initial pH	10.4	10.4
Final pH	9.5	9.5
H_2O_2, kg/t	30	30
NaOH, kg/t	30	30
Waterglass, kg/t	24	0
Stabilizer	0	PHAA
Dosage, kg/t	0	2

Dilution to Cs 5%

T, °C	50	50
t, min	15	15
Cs, %	5	5
pH	9.3	9.2
TOC, kg/t	21.0	19.3
COD, kg/t	58.9	51.1
Turbidity, NTU	301	233
Residual H2O2, kg/t	6.2	5.9

	Dewatering to Cs 30%		
Brightness, %ISO	77.6	77.5	
Water extract (SCAN-CM 44:97)			
Turbidity, NTU	24.8	32.1	Unbleached
COD, mg/l	310	360	pulp
Extractives is pulp			
Fatty acids, mg/kg	150	220	390
Resin acids, mg/kg	110	120	550
Lignans, mg/kg	10	13	130
Sitosterols, mg/kg	37	54	110
Steryl esters, mg/kg	230	430	720
Triglycerides, mg/kg	210	710	1300
Sum	747	1547	3200

The high turbidity of the filtrates after dilution can be attributed to extractives. The analysis of extractives show, that a major part of extractives was removed in bleaching. The results show also that silicate (waterglass) has some dispersing ability against extractives since the extractives content is much higher with acrylate-based stabilizer. This means that especially in the case on silicate-free bleaching, pitch dispersants are advantageous.

Example 1

A sample of CTMP-pulp (aspen) was taken from a mill and bleached with peroxide to brightness of 83-84% ISO. The bleaching conditions were as follows: t = 120 min, 70°C, consistency 30%, H_2O_2 38 kg/t, NaOH 21 kg/t, Na_2CO_3 8 kg/t. The pulp was already chelated in the mill and the manganese content was 1.5 ppm, Fe 5 ppm. The additives were dosed in the peroxide bleaching stage and after bleaching the pulp was diluted to 10% consistency at different pH levels, and subsequently dewatered. The table below shows the turbidity of the filtrate after dewatering. The experiment according to this invention was done using per ton dry pulp 2 kg polymer (poly-α-hydroxy acrylate) as stabilizer and 0.1 kg naphthalene sulphonate + 0.1 kg non-ionic surfactant (fatty alcohol ethoxylate 7 mole EO, C12-C14, HLB 12.3). In the comparative experiments waterglass and poly-α-hydroxy acrylate were used as stabilizers. The bleaching result and chemicals consumption was about the same in each case.

Waterglass, 25 kg/t		Acrylate polymer 2 kg/t		According to invention	
pH	Turbidity, NTU	pH	Turbidity, NTU	pH	Turbidity, NTU
6.6	1510	6.3	1353	6.5	1464
7.5	1430	7.3	1317	7.2	1440
7.8	1465	7.7	1389	7.5	1481

As can be seen from the results, silica originating from the waterglass (sodium silicate) increases turbidity. This may be attributed to higher extractives content in the filtrate. When silicate is replaced by a polymer-based stabilizer, turbidity is lower and thus extractives content in pulp is higher. The chemical composition according to this invention yields higher turbidity, which proves that the extractives dissolved in alkaline peroxide are not re-precipitated after dilution.

Example 2

A sample of CTMP-pulp (aspen) was taken from a mill and bleached with peroxide in high consistency. The bleaching conditions and results are shown in the table below. The surfactants were added in the bleaching stage, and after bleaching the pulp was diluted with ion-exchanged water. The composition of the surfactants here was naphtalene sulfonic acid condensation product (Na-salt) and fatty-alcohol ethoxylate (same as in previous example) in weight-ratio 2:1 (dosage as 20% water solution). The polymer-based stabilizer was a mixture of poly-alfa-hydroxyacrylate and maleate-acrylate copolymer (1:4 w:w) having a active substance content of 25%.

According to invention		P No	P No	P Yes	P Yes
t, min		120	120	120	120
T, °C		70	70	70	70
Cs, %		30	30	30	30
Initial pH		8.7	8.6	8.8	8.8
Final pH		8.4	8	8.4	8.3
Stabilizer, kg/t		2	2	2	2
Na_2CO_3, kg/t		8	8	8	8
NaOH, kg/t		21	21	21	21
H_2O_2, kg/t		38	38	38	38
Surfactant, kg/t		0	0	1	1
Polyvinyl alcohol, kg/t		0	1	0	1
Polyethyleneglycol, kg/t		0	1	1	0
Residual H_2O_2, kg/t		27.4	27.3	28.3	27.7
Brightness, %ISO	73.4	81.0	80.9	81.2	81.2
Dilution with ion-exchange water		↓	↓	↓	↓
t, min		10	10	10	10
T, °C		70	70	70	70
Cs, %		5	5	5	5
pH		8.2	8.1	8.2	8.3
Turbidity, NTU		608	607	627	651
DCM extract *, %		0.38	0.35	0.27	0.25

* from pulp

DCM stands for dichloromethane.

The results show, that the method according to the invention reduces extractives in the pulp and does not affect the bleaching result.

Example 3

A sample of CTMP-pulp (aspen) was taken from a mill and bleached with peroxide to brightness on 83-84% ISO. The surfactant additives were dosed in peroxide bleaching stage and after bleaching the pulp was diluted to 10% consistency at different pH levels, and subsequently dewatered. In one experiment a surfactant additive was also dosed after the dilution. The results are shown in the table below. The surfactant additives used here were naphtalenesulphonate condensation product (**A**) and fatty alcohol ethoxylate (**B**, 25 mole EO, C16-C18, HLB 16). The polymer-based stabilizer was a mixture of poly-alfa-hydroxyacrylate and maleate-acrylate copolymer (1:4 w:w) having a active substance content of 25%.

	P	P	P	P
t, min	120	120	120	120
T, °C	70	70	70	70
Cs, %	30	30	30	30
Initial pH	9	8.9	9	9
Final pH	8.5	8.3	8.5	8.3
Stabilizer, kg/t	0	2	2	2
Waterglass, kg/t	25	0	0	0
Na_2CO_3, kg/t	8	8	8	8
NaOH, kg/t	19	21	21	21
H_2O_2, kg/t	38	38	38	38
Additive	-	B	A	-
Dose kg/t	-	1	1	-

According to invention	**No**	**No**	**No**	**Yes**	**Yes**	**Yes**	**No**
t, min	60	60	60	60	60	60	60
T, °C	70	70	70	70	70	70	70
Cs, %	10	10	10	10	10	10	10
Initial pH	5.5	6.5	8.2	6.4	6.5	6.6	6.6
Final pH	5.6	6.6	7.9	6.4	6.5	6.8	6.6
Additive	-	-	-	-	A	-	-
Dose, kg/t	-	-	-	-	0.5	-	-
Residual, H_2O_2, kg/t	27.3	27.6	27.2	27.4	27.9	27.5	27.1
Brightness, %ISO	82.7	83.5	83.2	83.2	83.2	82.6	82.7
Extractive, mg/kg							
Fatty acids	550	470	530	410	420	430	490
Resin acids	170	140	130	120	120	130	130
Lignans	71	56	55	41	42	67	55
Sitosterols	8	6	7	3	3	8	7
Steryl esters	420	280	250	240	230	280	310
Triglycerides	1300	1010	940	810	800	980	1020
Sum	2519	1962	1912	1624	1615	1895	2012

The results show that the combination of polymer-based stabilizer and anionic and/or nonionic surfactant gives lower extractives content than waterglass.